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# Electrochemical Preparation and Applications of Copper(I) Acetylides: A Demonstration of How Electrochemistry Can Be Used to Facilitate Sustainability In Homogeneous Catalysis

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## **General Information:**

Solvents and reagents were purchased from suppliers and used without any further purification unless otherwise stated. Normal phase silica gel (Merck KGaA) and sand (VWR) were used for column chromatography. All reactions were monitored by TLC unless otherwise stated. TLC plates pre-coated with silica gel 60 F254 on aluminium (Merck KGaA) were used, detection by UV (254 nm) and chemical stain (potassium permanganate). Mass spectra were measured on Thermo Finnigan MAT900 XE and Waters LCT Premier XE machines operating in ESI mode. <sup>1</sup>H NMR spectra were recorded at 600 MHz and <sup>13</sup>C NMR spectra were recorded at 150 MHz on Bruker AMX spectrometers at ambient temperature. All chemical shifts were referenced to the residual proton impurity of the deuterated solvent. In <sup>1</sup>H NMR the multiplicity of the signal is indicated as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet), defined as all multipeak signals where overlap or complex coupling of signals makes definitive descriptions of peaks difficult. The <sup>13</sup>C NMR is assigned as C (quaternary), CH, CH<sub>2</sub> and CH<sub>3</sub> as determined by DEPT 135. Coupling constants are defined as J and quoted in Hz to one decimal place. Infrared spectra were obtained on a Bruker Alpha FTIR Spectrometer operating in ATR mode and peaks were assigned as 'w', 'm' or 's' denoting weak, medium or strong peaks respectively. Melting points were measured with a Gallenkamp apparatus and are uncorrected. In vacuo is used to describe solvent removal by Büchi rotary evaporation between 17-40 °C. For NMR experiments, CDCl<sub>3</sub> denotes deuterated  $(d_1)$  chloroform. Electrochemical reactions were carried out using an Ivium Technologies Vertex model potentiostat operating in chronoamperometry mode. CV plots were carried out using this same potentiostat with a glassy carbon working-electrode, a Pt wire counter-electrode and a Ag wire quasi reference-electrode.

## **Details of Electrochemical Methods:**

The general experimental setup we used for electrochemical reactions was designed to be as simple and accessible as possible. In doing so we hope to minimise the disparity and lack of reproducibility of results inherent in electro-organic synthesis due to there being a lack of standardised experimental setups. For all reactions we used a divided 'H' cell as our reaction vessel (dimensions shown in Figure S1) with each chamber having a size B19 ground-glass neck and a total volume of 20 mL. A semi-porous sintered glass divider sits between each chamber. All reactions were however carried out using 10 mL of electrolyte solution in each chamber as this was sufficient to sit above the line of the sintered glass divider and thus allow sufficient ion transfer. Copper electrodes were made by cutting strips from a roll of metallic copper sheet metal (around 0.5 mm thickness) to create plates with dimensions of 10 mm x 40 mm. When used, these were placed into solution to a depth of 25 mm, meaning the area of electrode exposed to solution was approximately 530 mm<sup>2</sup>. A silver wire, which was 1 mm thick, was used as a quasi referenceelectrode and was likewise placed into solution to a depth of 25 mm giving an effective area of 79 mm<sup>2</sup>. Both the copper plate and the silver wire were placed into the same chamber to minimise the potential drop deriving from resistance and kept 10 mm apart. A platinum wire of 1 mm thickness was used as the counter-electrode and placed in the other chamber of the H cell, this time at a depth of 40 mm giving an effective area of 126 mm<sup>2</sup>. Where graphite electrodes were used for the working-electrode and/or counter electrode, rods of 5 mm diameter were used at a depth of 25 mm giving an effective area of 412 mm<sup>2</sup>. Reactions were run using an Ivium Technologies Vertex model potentiostat operating in chronoamperometry mode. This model allowed for real-time charge over time and current over time graphs to be generated which we found exceedingly useful for this work, especially for measuring charge passed over the course of reactions.



Figure S1. Image of H Cell and electrodes used with dimensions

# **Electrochemical Preparation of Copper Acetylides:**

Various optimisation and control reactions are shown in Table S1.

Table S1. Optimisation and control reactions carried out to develop conditions<sup>a</sup>

	Cu Plate (Voltag Base Ph————————————————————————————————————	e) on ► Ph-==- 1	$Cu$ $O_2$ $Ph$	<u>=_</u> Ph ₂
Entry	Electrolyte Solution	Voltage	Base	Yield (%) <sup>b</sup>
1 <sup>c</sup>	0.05 M LiClO4/NH4OH : EtOH (5:3)	+2.00 V for 16 h	None <sup>d</sup>	21
2 <sup>c</sup>	NH₄OH : EtÓH (5:3) <sup>e</sup>	+0.50 V for 4 h	None <sup>d</sup>	9
3	0.10 M Bu4NPF6/MeCN	+0.50 V for 4 h	DABCO (2.0 eq)	92
4	0.10 M Bu <sub>4</sub> NPF <sub>6</sub> /MeCN	+0.50 V for 4 h	None	3
5	0.10 M Bu <sub>4</sub> NPF <sub>6</sub> /MeCN	+0.50 V for 2 h	DABCO (2.0 eq)	68
6	0.10 M Bu4NPF6/MeCN	+0.50 V for 4 h	DABCO (1.0 eq)	69
7	0.10 M Bu <sub>4</sub> NPF <sub>6</sub> /MeCN	No electricity used	DABCO (2.0 eq)	0
8 <sup><i>f</i></sup>	0.10 M Bu <sub>4</sub> NPF <sub>6</sub> /MeCN	+0.50 V for 4 h	DABCO (2.0 eq)	0 <sup><i>f</i></sup>

<sup>e</sup> In all cases 0.50 mmol phenylacetylene was used, except in Entry 1 where 2.00 mmol was used. All reactions were carried out using a Cu plate (5.30 cm<sup>2</sup> surface area) working-electrode, a Pt wire (1.26 cm<sup>2</sup>) counter-electrode and a Ag wire (0.79 cm<sup>2</sup>) quasi reference-electrode. <sup>b</sup> Isolated yield of copper acetylide 1. <sup>c</sup> Based on conditions reported by C. Theunissen et al.<sup>1</sup> <sup>d</sup> No base added as the electrolyte solution functioned as the base. <sup>e</sup> Ammonium hydroxide solution acted as the electrolyte. <sup>f</sup> Reaction mixture exposed to O<sub>2</sub> causing copper acetylide 1 to oxidise and form diyne 2 in 63% isolated yield.

# Control Experiment Using Purchased Cu(MeCN)<sub>4</sub>PF<sub>6</sub>:

Bu<sub>4</sub>NPF<sub>6</sub> (0.77 g, 2.0 mmol), Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (0.37 g, 1.0 mmol) and DABCO (0.11 g, 1.0 mmol) were added to a flame-dried flask backfilled with argon then dissolved in reagent grade MeCN (20 mL). The solution was then degassed for 5 min before phenylacetylene (0.06 mL, 0.55 mmol) was added dropwise. The solution was then degassed for a further 5 min before being left to stir at RT under argon for 2 h. The yellow precipitate was then collected by Büchner filtration and washed with MeCN (30 mL), then H<sub>2</sub>O (30 mL), then acetone (30 mL) to yield (phenylethynyl)copper, **1** as a bright yellow solid (72 mg, 0.43 mmol, 79%).

# General Electrochemical Procedure of Copper Acetylides:

Bu<sub>4</sub>NPF<sub>6</sub> (0.77 g, 2.0 mmol) was dissolved in reagent grade MeCN (20 mL) to make up a 0.1 M solution. A divided 'H' cell was charged with this solution (10 mL each side). A copper plate (5.30 cm<sup>2</sup> area) and a silver wire (0.79 cm<sup>2</sup> area) were then placed into one chamber, and a platinum wire (1.26 cm<sup>2</sup> area) was placed into the other chamber. These electrodes were connected up to a potentiostat (Cu = working-electrode, Ag = quasi reference-electrode, Pt = counter-electrode) and the voltage was set to run at +0.50 V for 4 h whilst stirring at RT and exposed to air. The voltage was then stopped and the pale green solution from the chamber containing the Cu electrode was transferred to a flame-dried round-bottomed flask and degassed with argon for 5 min. DABCO (1 mmol, 2 equiv) and the terminal alkyne (0.5 mmol, 1 equiv) were then added, immediately causing a yellow precipitate to form. The solution was then degassed for a further 5 min before being left to stir for 1 h at RT under argon. The yellow precipitate was then collected by Büchner filtration and washed with MeCN (30 mL), then H<sub>2</sub>O (30 mL), then acetone (30 mL) before being dried in a vacuum oven to yield the copper acetylide product.

# (Phenylethynyl)copper, 1



# ((3-Methoxyphenyl)ethynyl)copper



3-Ethynylanisole (0.06 mL, 0.47 mmol) used to yield a bright yellow solid (82 mg, 0.42 mmol, 89%); m.p. 186-188 °C (dec.); IR  $v_{max}$  (solid) 3064 (m), 2937 (m), 2830 (m), 1951 (m), 1934 (m), 1588 (s), 1482 (s), 1460 (s), 1414 (s), 1315 (s), 1261 (s), 1189 (s), 1147 (s), 1036 (s), 994 (s), 915 (s), 842 (s), 787 (s), 774 (s), 684 (s) cm<sup>-1</sup>.

# (p-Tolylethynyl)copper

*p*-Tolylacetylene (0.06 mL, 0.47 mmol) used to yield a bright yellow solid (76 mg, 0.43 mmol, 91%); m.p. 235-237 °C (dec.) (lit.,<sup>4</sup> 236 °C); IR  $\nu_{max}$  (solid) 3017 (w), 2915 (m), 1931 (w), 1887 (w), 1500 (s), 805 (s), 515 (s) cm<sup>-1</sup>. Data in agreement with literature.<sup>1,4</sup>

# (Thiophen-3-ylethynyl)copper



3-Ethynylthiophene (0.05 mL, 0.51 mmol) used to yield a bright yellow solid (56 mg, 0.33 mmol, 64%); m.p. 193-195 °C (dec.); IR  $v_{max}$  (solid) 3102 (w), 2926 (w), 2869 (w), 1936 (w), 763 (s), 621 (s) cm<sup>-1</sup>.

# (3-Ethoxy-3-oxoprop-1-yn-1yl)copper

## EtO<sub>2</sub>C-----Cu

Ethyl propiolate (0.05 mL, 0.49 mmol) used to yield a bright yellow solid (70 mg, 0.44 mmol, 88%); m.p. 182-184 °C (dec.); IR  $\nu_{max}$  (solid) 2983 (w), 2876 (w), 1954 (m), 1914 (m), 1694 (s), 1453 (w), 1194 (s), 1021 (s), 791 (s), 743 (s) cm<sup>-1</sup>.

## (4-Phenylbut-1-yn-yl)copper



4-Phenyl-1-butyne (0.07 mL, 0.50 mmol) used to yield a bright yellow solid (62 mg, 0.32 mmol, 64%); m.p. 174-176 °C (dec.); IR  $\nu_{max}$  (solid) 3055 (w), 2929 (w), 1941 (w), 1605 (w), 1496 (m), 1451 (m), 1436 (m), 764 (s), 688 (s), 461 (s) cm<sup>-1</sup>.

# (Cyclohex-1-en-1-ylethynyl)copper



1-Ethynylcyclohexene (0.06 mL, 0.51 mmol) used to yield a dark yellow solid (63 mg, 0.37 mmol, 73%); m.p. 163-165 °C (dec.); IR  $\nu_{max}$  (solid) 2926 (m), 2855 (m), 1433 (w), 833 (s), 793 (s), 556 (s) cm<sup>-1</sup>.

# ((Trimethylsilyl)ethynyl)copper

Me<sub>3</sub>Si-----Cu

Trimethylsilylacetylene (0.07 mL, 0.51 mmol) used to yield an orange-red solid (60 mg, 0.37 mmol, 73%), stored at -20 °C to prevent decomposition; m.p. 142-144 °C (dec.); IR  $v_{max}$  (solid) 2955 (w), 2895 (w), 2189 (w), 2139 (w), 1878 (w), 1245 (m), 839 (s), 757 (m), 668 (m) cm<sup>-1</sup>.



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### **Copper Oxidation State Determination Experiments:**

#### Reaction Using Asymmetric Electrodes:

A graphite rod working-electrode (4.12  $\text{cm}^2$  area) was first coated with a layer Cu by placing it into an undivided cell containing a 0.5 M CuSO<sub>4(aq.)</sub> solution. A Ag wire quasi reference-electrode (0.79 cm<sup>2</sup> area) and a Pt wire counter-electrode (1.26  $\text{cm}^2$  area) were added and all electrodes were then connected up to a potentiostat. The voltage was set to -0.50 V for 400 s (13.40 C passed, 69.45 µmol, 4.41 mg Cu deposited). These electrodes were then carefully cleaned with water and acetone and placed into a divided 'H' cell (Cu-coated graphite and Ag wire in one chamber, Pt wire in the other chamber) which had been charged with a 0.1 M solution of Bu<sub>4</sub>NPF<sub>6</sub> (0.77 g, 2.0 mmol, 2.0 eq) dissolved in reagent grade MeCN (20 mL) (10 mL each side of H cell). The electrodes were then connected up to a potentiostat (Cu-coated graphite = WE, Ag = RE, Pt = CE) and the voltage was set to run at +0.50 V for 30 min whilst stirring at RT and exposed to air (6.17 C passed). The voltage was then stopped and the pale green solution from the chamber containing the working-electrode was transferred to a flame-dried round-bottomed flask and degassed with argon for 5 min. DABCO (0.11 g, 1.0 mmol, 2.0 eq) and phenylacetylene (0.06 mL, 0.55 mmol, 1.0 eq) were then added, immediately causing a vellow precipitate to form. The solution was then degassed for a further 5 min before being left to stir for 2 h at RT under argon. The yellow precipitate was then collected by Büchner filtration and washed with MeCN (30 mL), then H<sub>2</sub>O (30 mL), then acetone (30 mL) before being dried in a vacuum oven to yield (phenylethynyl)copper, 1 as a bright yellow solid (8.1 mg, 49.19 µmol, 71% efficiency of copper atom integration into product). Value for z by rearranging the Faraday equation (Eq. (1) in main text) =  $6.17 / (0.00004919 \times 1.602 \times 10^{-19} \times 6.022 \times 10^{23}) = 1.30$ .

#### Reaction Using Symmetrical Electrodes:

A graphite rod working-electrode (4.12  $\text{cm}^2$  area) was first coated with a layer Cu by placing it into an undivided cell containing a 0.5 M CuSO<sub>4(aq.)</sub> solution. A Ag wire quasi reference-electrode (0.79 cm<sup>2</sup>) area) and a graphite rod counter-electrode (4.12 cm<sup>2</sup> area) were added and all electrodes were then connected up to a potentiostat. The voltage was set to -0.50 V for 500 s (12.51 C passed, 64.56 µmol, 4.10 mg Cu deposited). These electrodes were then carefully cleaned with water and acetone and placed into a divided 'H' cell (Cu-coated graphite and Ag wire in one chamber, other symmetrical graphite rod in the other chamber) which had been charged with a 0.1 M solution of Bu<sub>4</sub>NPF<sub>6</sub> (0.77 g, 2.0 mmol, 2.0 eq) dissolved in reagent grade MeCN (20 mL) (10 mL each side of H cell). The electrodes were then connected up to a potentiostat (Cu-coated graphite = WE, Ag = RE, other graphite rod = CE) and the voltage was set to run at +0.50 V for 30 min whilst stirring at RT and exposed to air (5.37 C passed). The voltage was then stopped and the pale green solution from the chamber containing the working-electrode was transferred to a flame-dried round-bottomed flask and degassed with argon for 5 min. DABCO (0.11 g, 1.0 mmol, 2.0 eq) and phenylacetylene (0.06 mL, 0.55 mmol, 1.0 eq) were then added, immediately causing a yellow precipitate to form. The solution was then degassed for a further 5 min before being left to stir for 2 h at RT under argon. The yellow precipitate was then collected by Büchner filtration and washed with MeCN (30 mL), then H<sub>2</sub>O (30 mL), then acetone (30 mL) before being dried in a vacuum oven to yield (phenylethynyl)copper, 1 as a bright yellow solid (8.2 mg, 49.80 µmol, 77% efficiency of copper atom integration into product). Value for z in rearranged Faraday equation (Eq. (1) in main text)  $= 5.37 / (0.00004980 \times 1.602 \times 10^{-19} \times 6.022 \times 10^{23}) = 1.12.$ 

## **Diyne Preparations; Without TMEDA and With TMEDA for Cu Recovery:**

## Method 1; Procedure for Ligand-Free Electrochemical Divne Formation:

A graphite rod working-electrode (4.12  $\text{cm}^2$  area) was first coated with a layer Cu by placing it into an undivided cell containing a 0.5 M CuSO<sub>4(aq.)</sub> solution. A Ag wire quasi reference-electrode (0.79 cm<sup>2</sup> area) and a Pt wire counter-electrode (1.26 cm<sup>2</sup> area) were added and all electrodes were then connected up to a potentiostat. The voltage was set to -0.50 V for 600 s (14.14 C passed, 73.29 µmol, 4.66 mg Cu deposited). These electrodes were then carefully cleaned with water and acetone and placed into a divided 'H' cell (Cu-coated graphite and Ag wire in one chamber, Pt wire in the other chamber) which had been charged with a 0.05 M solution of Bu<sub>4</sub>NPF<sub>6</sub> (0.39 g, 1.0 mmol, 1.0 eq) dissolved in reagent grade DCM (20 mL) (10 mL each side of H cell). The electrodes were then connected up to a potentiostat (Cu-coated graphite = WE, Ag = RE, Pt = CE) and the voltage was set to run at +0.50 V for 30 min whilst stirring at RT and exposed to air. Phenylacetylene (0.11 mL, 1.0 mmol, 1.0 eq) was then added to the chamber containing the graphite and silver electrodes, followed by DABCO (0.13 g, 1.2 mmol, 1.2 eq). The potentiostat was set to run at +0.50 V for a further 2.5 h whilst stirring at RT, then the solution was left to stir for a further 13 h whilst exposed to air. The solution was then filtered into a separating funnel and extracted once with brine (30 mL), before the aqueous layer was diluted with DCM (30 mL). The organic layer was extracted and combined with the other organic layer, then washed once with  $H_2O$  (30 mL), dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The resulting yellow solid was dissolved in 20% EtOAc/pet. ether, and passed through a plug of silica gel to give the product 2 as a white crystalline solid (69 mg, 0.34 mmol, 68%).

## Method 2; Procedure for TMEDA-Assisted Diyne Formation and Electrochemical Cu Recovery:

A graphite rod working-electrode (4.12  $\text{cm}^2$  area) was first coated with a layer Cu by placing it into an undivided cell containing a 0.5 M CuSO<sub>4(aq.)</sub> solution. A Ag wire quasi reference-electrode (0.79 cm<sup>2</sup>) area) and a Pt wire counter-electrode (1.26 cm<sup>2</sup> area) were added and all electrodes were then connected up to a potentiostat. The voltage was set to -0.50 V for 600 s (11.99 C passed, 62.14 µmol, 3.95 mg Cu deposited). These electrodes were then carefully cleaned with water and acetone and placed into a divided 'H' cell (Cu-coated graphite and Ag wire in one chamber, Pt wire in the other chamber) which had been charged with a 0.05 M solution of Bu<sub>4</sub>NPF<sub>6</sub> (0.39 g, 1.0 mmol, 1.0 eq) dissolved in reagent grade DCM (20 mL) (10 mL each side of H cell). TMEDA (0.15 mL, 1.0 mmol, 1.0 eq) was then added to the chamber containing the Cu and the electrodes were connected up to a potentiostat (Cu-coated graphite = WE, Ag = RE, Pt = CE). The voltage was set to run at +0.50 V for 30 min whilst stirring at RT and exposed to air. At the end of this time all Cu had been released from the graphite electrode and the solution was pale blue. Phenylacetylene (0.11 mL, 1.0 mmol, 1.0 eq) was then added to the chamber containing the graphite and silver electrodes, followed by DABCO (0.14 g, 1.2 mmol, 1.2 eq). The potentiostat was set to run at +0.50 V for a further 2.5 h whilst stirring at RT, then the solution was left to stir for a further 13 h whilst exposed to air. H<sub>2</sub>O (20 mL) was then added to the solution and stirred vigorously for 1 h, causing the Cu species to migrate into the aqueous phase. The two layers were separated into the aqueous layer and the organic layer:

The dark blue aqueous layer was treated with 2 M  $HCl_{(aq.)}$  (3 drops) and then placed into one side of an H cell, along with NaCl (0.20 g, 3.42 mmol). The other chamber was filled with a slightly acidic (2 M  $HCl_{(aq.)}$  (3 drops)) brine solution (NaCl (0.20 g, 3.42 mmol) dissolved in H<sub>2</sub>O (20 mL)) and the H cell was charged with a graphite rod working-electrode, a Ag wire quasi reference-electrode and a Pt wire counter-electrode (graphite and silver in copper solution chamber, platinum in brine-only chamber). The electrodes were then connected up to a potentiostat and the voltage was set to run at -1.00 V for 30 min, causing Cu metal to once more be plated onto the surface of the graphite rod. To accurately determine

how much copper had been recovered, this Cu-coated graphite rod was used as a working-electrode when placed into an H cell charged with a 0.1 M (Bu<sub>4</sub>NPF<sub>6</sub> (0.77 g, 2.0 mmol) dissolved in reagent grade MeCN (20 mL)) solution (10 mL each side). A silver wire quasi reference-electrode was added to the same chamber as the Cu-coated graphite electrode and a platinum wire counter-electrode was placed into the other chamber, before all electrodes were connected up to a potentiostat and the voltage was set to run at +0.50 V for 1800 s at RT and exposed to air (2.34 C passed, 24.26  $\mu$ mol, 1.54 mg Cu recovered, 39%).

The organic layer was washed once with  $H_2O$  (30 mL), dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The resulting yellow solid was dissolved in 20% EtOAc/pet. ether. and passed through a plug of silica gel to give the product **2** as a white crystalline solid (71 mg, 0.35 mmol, 70%).

# 1,4-Diphenylbuta-1,3-diyne, 2



Yields obtained by Methods 1 and 2 stated above; m.p. 86-88 °C (lit.,<sup>5</sup> 86-88 °C); R<sub>f</sub> 0.54 (20% EtOAc/pet. ether.); IR  $\nu_{max}$  (solid) 3047 (w), 2143 (w), 1483 (m), 1438 (m), 914 (m), 751 (s), 682 (s), 523 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta_{H}$  7.53-7.55 (4H, m, Ar*H*), 7.33-7.40 (6H, m, Ar*H*) ppm; <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta_{C}$  132.6 (*C*H), 129.3 (*C*H), 128.6 (*C*H), 121.9 (*C*), 81.7 (*C*), 74.0 (*C*) ppm; LRMS (ESI) m/z 203 ([M+H]<sup>+</sup>, 6%), 201 (48%), 199 (100%). Data in agreement with literature.<sup>5</sup>







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